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Optical and luminescence characteristics of YAG:Ce crystals grown by horizontal directed crystallization in reducing gas medium

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The optical and luminescence characteristics of YAG:Ce crystals grown first using the gas phase horizontal directed crystallization in reducing gas media developed by the authors have been studied. A correlation has been found between the cerium content and intensity of the absorption bands peaked at 235, 270 nm and in the 250–300 nm range. A model is proposed to describe the optical absorption features of YAG:Ce crystals grown in reducing conditions. According to the model, in the presence of cerium ions, the conversion of F, F^+ centers occurs. The luminescence spectra are characterized, besides of a wide (530–540 nm) Ce^{3+} ion band, by a 400 nm band which is due to F centers.

Исследованы оптические и люминесцентные характеристики кристаллов YAG:Ce, впервые полученных с использованием разработанных авторами газовых технологий горизонтальной направленной кристаллизации в восстановительных средах. Установлена корреляция содержания церия в кристаллах и интенсивности полос поглощения при 235, 370 нм и в области 250–300 нм. Предложена модель, описывающая особенности оптического поглощения кристаллов YAG:Ce, выращенных в восстановительных условиях. Согласно этой модели, в присутствии ионов церия происходит конверсия F, F^+-центров. Спектры люминесценции характеризуются, кроме широкой полосы (530–540 нм) ионов Ce^{3+}, линией 400 нм, за которую ответственны F-центры.

The horizontal directed crystallization (HDC) is among the most effective methods in growing of large crystals. The development of novel gas phase HDC techniques [1, 2] made it possible to expand considerably the potential of that method. The main advantages of those techniques are based on the use of carbon-graphite construction materials providing a rather simple control of thermal field and temperature gradient distribution in the growing crystal. The pressure and reducing potential of the gas medium provides the protection of the furnace materials and reduction of mass transfer therein. The crystallization in the zone melting mode makes it possible to grow crystals at a rather high homogeneity of the activator distribution along the crystal. The transversal concentration gradient in the crystal is substantially zero in this case. Thus, the gas phase HDC techniques are of good promise in the growth of large scintillation crystals, in particular, of cerium activated ones, since the reducing growing conditions favor the introduction of cerium in the Ce^{3+} state. This work presents the study results of optical absorption and luminescence of activated YAG:Ce crystals prepared first using the gas phase HDC technique in reducing atmosphere.

The crystals were grown in a furnace provided with tungsten heater and carbon-

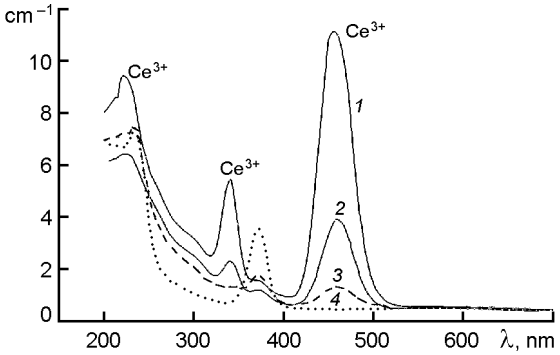

Fig. 1. Absorption spectra of YAG crystals with various Ce concentrations. Curves *1*, *2*, *3* correspond to 1.0; 0.3; and 0.1 wt % CeO_2 content in the blend, respectively; curve *4* is for undoped YAG.

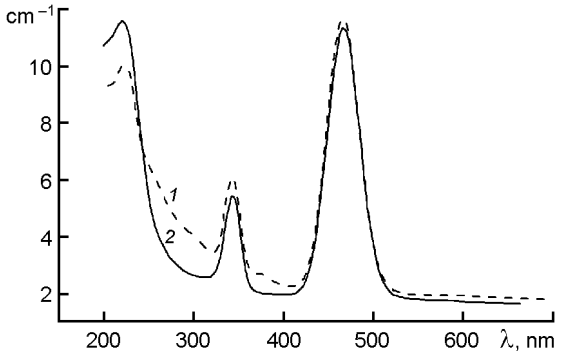

Fig. 2. Effect of oxidative annealing on the YAG:Ce optical absorption (*1*, prior to air annealing; *2*, thereafter).

graphite thermal insulation in reducing CO and H_2 atmosphere at 5 to 15 Pa pressure. The growth medium was formed in the growth furnace spontaneously due to interaction of the melt vapor and residual gases with the carbon of the insulation; its pressure was defined by the furnace pumping-out rate provided by a mechanical pump [3]. The broken $Y_3Al_5O_{12}$ crystals and CeO_2 powder (0.1 to 1 wt. % in the blend) were loaded into a molybdenum crucible. The crystal pulling speed was 1 to 2 mm/h. Non-activated YAG crystals were grown also for comparison purpose. The double-side polished plates of $30\times30\times1$ mm^3 and $30\times30\times5$ mm^3 were prepared from the same areas of the crystals obtained. The transmission spectra were recorded using a Specord UV-VIS spectrophotometer; the luminescence ones, using a SDL-2 spectrophotometer, a DKSSh150 xenon lamp being used as the excitation source.

The grown YAG:Ce crystals ($120\times90\times30$ mm^3) exhibit a homogeneous yellow-green coloration while the non-activated ones are essentially colorless (a weak lilac tint). No inclusions or a visible streakiness are observed within the crystal volume. Fig. 1 presents the absorption spectra of the crystals containing various cerium concentrations. It follows from the spectra that the YAG:Ce crystals show absorption bands at 227, 235, 340, 370, 458 nm as well as a wide band in the 250 to 300 nm range with weak-resolved peaks therein. The 227, 340 and 458 absorption bands correspond to the $4f^1 \rightarrow 5d^1$ transition in Ce^{3+} ions within the YAG lattice [4, 5]. Since the crystals were grown in a reducing medium, the intense band at 370 nm may be due to absorption of intrinsic color centers based on anionic vacancies of F, F^+ center type. The judgements on its nature are still ambiguous. In particular, it is supposed that the 370 nm band is due by the growth defects resulting from the melt stoichiometry distortions and is associated with capturing of the crystal-forming cations in the interstices [6, 7]. On the other hand, the studied carried out in [5] evidence that the 235 and 370 nm bands result most likely from the anionic non-stoichiometry of yttrium-aluminum garnet. The two weak-resolved peaks in the 250–300 nm region are neatest to the 255 nm absorption band corresponding to the charge-exchange transition of Fe^{3+} [8] as well as to the 295 nm one of an unestablished nature [9].

Comparison of the spectra (Fig. 1) shows that as the cerium concentration rises, the absorption in the 235 and 370 nm bands decreases while increasing in the 250–300 nm region. Thus, it can be supposed that heterovalent cerium ions may assist in the color center conversion. The following process is possible in the reducing growth conditions:

$$Ce^{4+} + F \rightarrow Ce^{3+} + F^+,$$

where a fraction of F centers is converted into F^+ ones. Then, the 235 and 370 nm bands must correspond to F centers and the absorption in the 250–300 nm region must be associated with F^+ ones. To check the connection between the color centers and anionic non-stoichiometry, the samples were annealed in an oxidizing medium, i.e. in air at 1300°C for 12 h (see Fig. 2). It has been established that the annealing results in a considerably decreased absorption at 235,

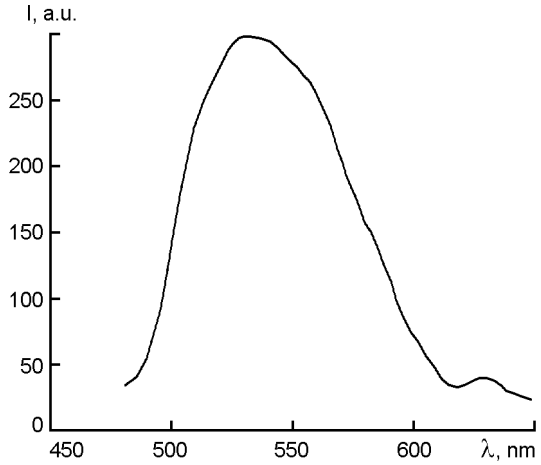

Fig. 3. YAG:Ce luminescence spectrum under excitation at 340 nm.

370 nm as well as in the 250–300 nm, so that the spectrum contains only cerium absorption bands. It is known that an anneal in oxidizing medium must cause an increased or at least unchanged absorption intensity of Fe^{3+} ions at 255 nm [8]. Moreover, the comparison of the spectra in Fig. 1 shows that the absorption mentioned is most pronounced in cerium-doped crystals only and is absent in undoped YAG ones. Since the growing was carried out in reducing atmosphere, the absorption near 250 nm in YAG:Ce crystals can be supposed to be due to a complex activator-vacancy center of Ce^{3+}–*F* type.

To study the luminescence spectra of grown crystals, those were excited to the 340 nm absorption band of cerium ions as well as at 265 nm to excite a defect-induced luminescence in the UV spectral region due to the presence of anti-site defects of Y_{Al}^{3+} type [10]. The obtained spectra (Figs. 3, 4) are characterized by a wide luminescence band of Ce^{3+} ions at 500–600 nm and a band near 400 nm that is to be ascribed to the centers absorbing at 235 and 370 nm, as is shown by the study of excitation spectra [9]. Thus, in our opinion, the luminescence at 400 nm is defined by the *F* centers. The luminescence maximum of cerium ions (530–540 nm) for the crystals grown in a reducing medium is shifted a little towards shorter wavelengths. This is connected most likely with changes in the cerium ion neighborhood due to anionic non-stoichiometry of yttrium-aluminum garnet. The intrinsic luminescence of YAG caused by the anti-site

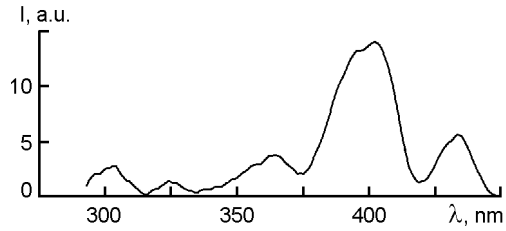

Fig. 4. YAG:Ce luminescence spectrum under excitation at 265 nm in the defect luminescence region.

defects was not revealed substantially in the samples studied (Fig. 4). This might be due to the possible falling of the 340 nm cerium absorption band into the defect luminescence of YAG:Ce and its quenching resulting from the anionic non-stoichiometry of the crystals.

To conclude, cerium activated YAG single crystals free of any inclusions and visible inhomogeneities of the activator distribution have been grown by the HDC method in a reducing gas medium at 5 to 15 Pa pressure. The crystals show absorption bands at 235 and 370 nm as well as a wide absorption band in the 250 to 300 nm range with weak-resolved peaks therein besides of cerium ion absorption bands. The absorption intensity in those bands has been established to be in a correlation with cerium content. A model is proposed to describe the transformation of absorption spectra yttrium-aluminum garnet crystals grown in a reducing medium. According to the model, as the cerium concentration increases, the conversion *F*, F^+ centers occurs as well as the formation of activator-vacancy complexes is possible. It has been shown that the absorption within the 250–300 nm region may be due to the F^+ centers. The 235 and 370 nm bands correspond to *F* centers. The absorption spectra of YAG:Ce crystals annealed in oxidizing conditions are shown to contain only the Ce^{3+} bands. The luminescence spectrum of the grown YAG:Ce crystals includes, besides of a wide band of Ce^{3+} ions, a peak near 400 nm which corresponds to the *F* center luminescence.

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Оптичні та люмінесцентні характеристики кристалів YAG–Ce, що вирощені методом горизонтальної направленої кристалізації у відновлювальному газовому середовищі

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Досліджено оптичні та люмінесцентні характеристики кристалів YAGЖ–Ce, вперше одержаних з застосуванням розроблених авторами газових технологій горизонтальної напрямної кристалізації у відновлювальних середовищах. Встановлено кореляцію вмісту церію у кристалах та інтенсивності смуг поглинання при 235, 370 нм та в області 250–300 нм. Запропоновано модель, яка описує особливості оптичного поглинання кристалів YAG:Ge, що вирощені у відновлювальних умовах. Згідно з цією моделлю, у присутності іонів церію відбувається конверсія F, F^+-центрів. Спектри люмінесценції характеризуються, окрім широкої (530–540 нм) смуги іонів Ce^{3+}, лінією 400 нм, зумовленою F-центрами.